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NATURAL MECHANISMS OF MECHANOCHEMICAL INTERACTIONS IN OXIDE POWDERS

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The effect of hydroxyl and other functional groups on mechanochemical interactions in oxide powders is shown. The general rules of non-covalent mechanochemical synthesis are established. Phenomenological models are discussed and the kinetic equations of mechanochemical synthesis are presented.

Key words: mechanochemical synthesis, oxide powders.

Chemical interactions in oxide powders are usually conducted at high temperatures [1]. The rate of interaction in a solid phase is significantly limited by diffusion through the product layer [1, 2]. The attractiveness of mechanochemical activation (MCA) apparently lies in the simplicity of its implementation as well as in the fact that comminution is in practice mandatory in oxide materials technology, while mills are some of the most widely used apparatus for effectuating mechanical excitation [2 – 4]. During MCA the process is accompanied by the formation and renewal of interparticle contact zones, the formation and migration of defects and the development of plastic deformations, which is completed by mixing components at the cluster and atomic levels [5].

Mechanochemical activation of individual components or their mixtures makes it possible to obtain the following advantages [2 – 5]:

– soften the conditions of synthesis by conventional methods;

– improve the operational properties of ready articles;

– synthesize new chemical compounds at subsequent stages as well as directly in the mill.

The thermodynamic possibility of chemical and other interactions during mechanical loading in a mill is determined by the change in the Gibbs free energy ΔG [6, 7]. Repeated attempts at making quantitative estimates of the pressure and temperature during mechanochemical processes did not yield constructive results [5]. Serious difficulties arise in determining the changes in the enthalpy ΔH and entropy ΔS. The

quantity ΔS increases especially as a result of the deformation of the crystal lattice during MCA, which in individual cases can even cause ΔG to change sign [3].

Devices that according to [3, 4] can be divided into three groups are used for MCA:

1) mills with impact action;

2) apparatus with a shear load;

3) mills with combined loading (impact – pressure – shear), in which the ratio between different types of actions is determined by the construction of the apparatus.

A general feature of these devices is an impulsive action associated with the mechanical motion of the working organs and material during processing in a mill. Another feature is the local character of the loading [2 – 4].

Mills of the third type are most widely used to conduct mechanochemical synthesis (MCS) [2, 3, 8]. In these devices high intensity mechanical action and tight interparticle contact are created, thereby creating the optimal conditions for solid-phase interactions.

Most classical attempts at MCS have focused on obtaining the desired product directly in the mill chamber [2]. They revealed serious drawbacks, such as unacceptably large energy consumption and contamination of the product of interaction [3]. This is especially important when using oxide powders with comparatively low chemical activation and quite high crystal hardness. MCS inevitably shifted toward softer conditions in order to attract industry [2].

To soften the conditions for MCS solid acids and bases, salts, can be used instead of water-free oxides. These compounds possess high chemical activity owing to the large difference between the electro-negativity and the acid-base properties. In addition, the free water released when they interact changes the reaction path and facilitates the diffusion of

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TABLE 1. Genesis of the Phase Composition of the Systems $Al(OH)_3$–KOH (Molar Ratio $Al_2O_3 : K_2O = 9 : 1$)

Initial mixture	Mechanical activation*	Calcination* at 1250°C
$Al(OH)_3$ (gibbsite) KOH	$Al(OH)_3$ (gibbsite) $Al(OH)_3$ (bayerite) $KAlO_2 \cdot 3H_2O$ KOH	$(Al_2O_3)_{16}$ $K_2Al_{18}O_{28}$ $KAl_{11}O_{17}$
Al_2O_3 KOH	Al_2O_3 KOH $KAlO_2 \cdot 3H_2O$	Al_2O_3 $KAl_{11}O_{17}$ $K_2Al_{18}O_{28}$

* The order of the phases in the table corresponds to their amount in the sample.

TABLE 2. Parameters of Thermal Synthesis (1200°C) of Aluminum Titanate and Cordierite from Stoichiometric Mixtures Subjected to MCA
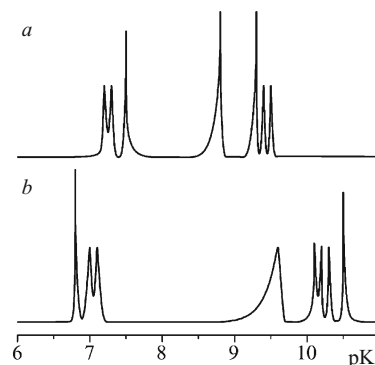
Final product	Initial mixture	Induction period τ_{ind}, min	Half-transformation period $\tau_{1/2}$, min
Aluminum titanate Al_2TiO_5	H_2TiO_3 $Al(OH)_3$	20 – 25	60 – 65
	TiO_2 Al_2O_3	25 – 30	125 – 130
Cordierite $Mg_2Al_4Si_5O_{18}$	$Al(OH)_3$ $Mg(OH)_2$ $SiO_2 \cdot nH_2O$	60 – 70	275 – 280
	Kaolinite Talc Hydrargillite	5 – 10	55 – 60

Fig. 1. pK spectra of the compositions of kaolin clay and dolomite after MCA in a vibratory mill, conducted by separated (*a*) and combined (*b*) methods.

reagents. MCS performed under such conditions is called soft mechanochemistry [2, 6].

The use of hydrated and water-free oxides for MCS gives products with different phase compositions [2, 9]. This is due to the differences in the composition of the powders after combined MCA (Table 1). Here, the formation of potassium hydroaluminate, and not only the presence of aluminum hydroxide, affects the subsequent transformations.

The hydrated raw material used at the MCA stage also affects the kinetics of the subsequent thermal synthesis; this is shown for the example of obtaining aluminum titanate (Table 2) [10]. The positive effect of soft conditions for MCA manifests much more strongly in the synthesis of multicomponent compounds [2, 11], specifically, cordierite. The synthesis of such compounds proceeds via the formation of intermediate phases (such as spinel, silicates, aluminosilicates), and the use of precursors containing such compounds makes it possible to reduce several-fold the induction period and the half-transformation time (see Table 2).

With simultaneous MCA the acid-base interaction has a large effect on the course of the process. For example, in obtaining a composite material from kaolin clay and dolomite,

depending on the method of MCA, differences are observed not only in the change in the particle size of the solid phase but also in the interaction of acid and base surface centers [12]. When the indicated mixture is subjected to MCA at the same time the intensity of the surface centers is leveled, as the data from pK-spectroscopy attest (Fig. 1).

During the investigation of mechanochemical processes in a system comprised of calcium compounds and aluminum hydroxide it was established that calcium hydroaluminates are formed when CaO and $Al(OH)_3$ are used, while in a mixture of $CaCO_3$ and $Al(OH)_3$ the predominant process is dispersion of aluminum hydroxide to particle size of the order of 60 nm (Fig. 2). $Ca(OH)_2$ occupies an intermediate position in this series.

It is shown in [13] that the penetration depth of chemical reactions during MCS correlates with an increase in the difference of the acid-base properties of the ingredients (Fig. 2), and the reduction of the size of the region of coherent scattering (CSR) of the $Al(OH)_3$ particles correlates with the hardness of the calcium compounds.

However, under soft conditions MCS does not always give the desired result. For example, in an attempt to synthesize zeolite of the type NaA from kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and sodium hydroxide using MCA the final products were nepheline or other sodium aluminates with a close-packed structural motif [14]. Preliminary dehydration of the kaolin made it possible to obtain sodalite with a cubic crystal lattice [15, 16]. It was shown in the same works that successful synthesis of zeolite with a crystal frame structure requires that sodium aluminates with the cubic or tetragonal system form at the MCA stage.

We showed in [8] that there exists an optimal MCA time, which was determined from the change in the energy efficiency of the process. Also, the optimal process time was determined for MCS of zeolite [15, 16]. In the present case this time is determined by the chemical processes occurring in the mill. IR spectroscopy shows (Fig. 3) that after MCA of the initial mixture absorption bands are observed in the spectra in the interval $500 – 420 \ cm^{-1}$, which are characteristic
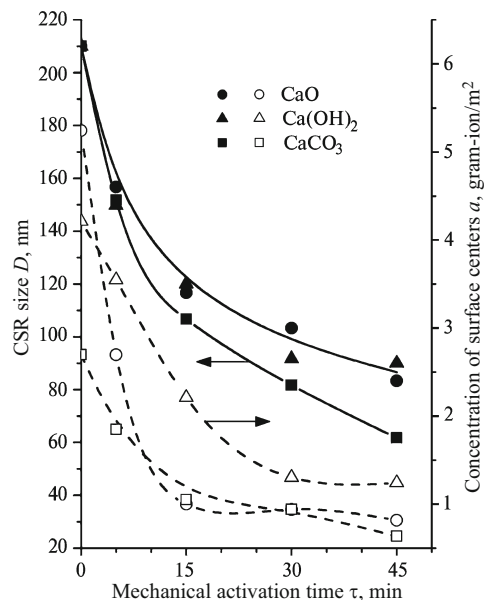
Fig. 2. Variation of the CSR size and concentration of the main centers in mixtures of calcium compounds and hydrargillite (molar ratio $CaO : Al_2O_3 = 1 : 1$) in the process of MCA in a vibratory mill.

Fig. 3. IR spectra of the systems metakaolin – sodium hydroxide – aluminum oxide (molar ratio $Al_2O_3 \cdot 2SiO_2 : NaOH : Al_2O_3 = 1 : 2 : 0.5$) after MCA in a vibratory mill. MCA times 5 min (a) and 15 min (b).

of deformation vibrations of the T–O bonds (where T = Si or Al atom). Absorption bands corresponding to symmetric and antisymmetric stretching vibrations of double rings are also observed in the region $600 - 500$ cm^{-1}. This makes it possible for us to talk about the fact that the bonds required for the formation of zeolite form even at the MCA stage. For a prolonged (15 min) MCA process in a rolling-ring vibratory mill a new absorption band appears in the absorption spectrum in the range $2400 - 2300$ cm^{-1}; this band is due to the possible hydrolysis of the framework bonds of the hydroxyl end groups. Thus, the MCS process (if this expression is admissible) becomes soft, which results in the formation of more closely packed sodalite.

The characteristics of 'covalent' and 'noncovalent' synthesis processes are compared in [17, 18]. Strong covalent bonds are formed in the first case and kinetically reversible ionic, hydrogen and similar bonds are form in the second case. The most important difference is that in 'covalent synthesis' the enthalpy change predominates in the Gibbs free energy, while in 'noncovalent synthesis' the enthalpy and entropy changes are comparable. Therefore, to obtain products by covalent synthesis the course and final result of the process are determined by the change in the energy state of the system and the result of 'noncovalent synthesis' will depend on the conditions of the process.

The examples presented in the present article of the MCS of different aluminates, cordierite and aluminum titanate are characteristic representatives of 'covalent synthesis'. To implement these synthesis processes it is best to use a mixture of components containing structural water and having large differences in the electronegativity and acid-base properties [2, 6]. 'Covalent' MCS requires mills that supply mechanical
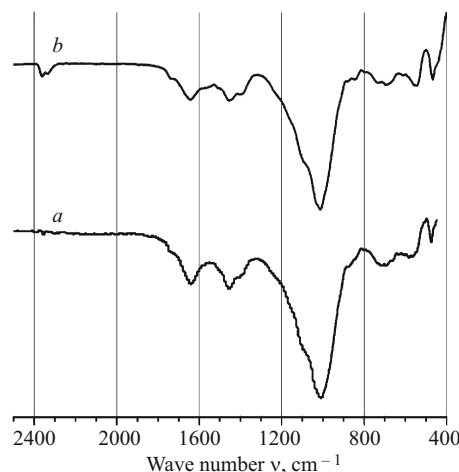
energy at a high level [3]. The MCS of zeolites, which are typical representatives of 'noncovalent synthesis', require very careful selection of the initial components and their ratios and of the equipment used for activation [15, 16].

The analysis and generalization of representative examples as well as a wide range of published data (many sources are not presented in here) have made it possible to propose possible phenomenological models of MCS. Since the mechanical action in different types of mills has its own characteristics and is of an impulsive character [4, 8], it is impossible to propose a universal model of MCS. These models are based on the idea that the acceleration of solid-phase interactions, the possibility of synthesis of new compounds at low temperatures and other processes observed in activating mills are due to deformation mixing of the components at the atomic and cluster levels [2 – 6]. In our view the physical picture of mechanochemical processes will be determined by the hardness of the crystals and the structural particulars of the lattice.

In the case of combined MCA of the components, in which the crystals have comparable hardness, when two particles collide under the action of the milling bodies mutual fracturing of the surface layers to nanosize crystallites and clusters and their displacement occur (Fig. 4a) [2, 3]. At subsequent stages of mechanical processing new phases form owing to plastic deformation. Chemical reactions occur inside secondary aggregates at the interparticle contacts.

In another case of MCS the crystals of the components used as reagents, for example, aluminum oxide and calcium [19] or potassium [20] hydroxide, have strongly differing hardness. In comparing the data on the size change and defect density of the Al_2O_3 crystallites it can be supposed that under the action of a mechanical impulse the softer components undergo size reduction into particles of harder alumi-
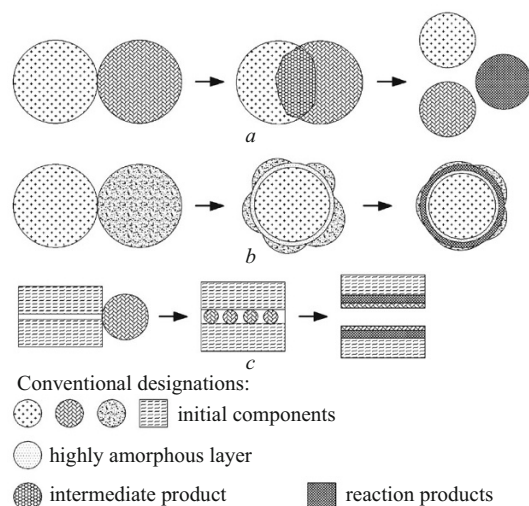
Conventional designations:

⬡ ⬡ ⬡ ▦ initial components

◯ highly amorphous layer

◉ intermediate product   ▨ reaction products

Fig. 4. Phenomenological models of MCS (see explanations in text): *a*) the crystals have comparable hardness; *b*) the crystal have different hardness; *c*) one of the crystals has a layered structure.

num oxide (Fig. 4*b*). The outer, strongly deformed, highly active layer enters quite easily into chemical interaction in which new compounds are formed. At subsequent stages deformation mixing facilitates the activation of the diffusion of the ingredients through a layer of the product.

Situations where one of the components possesses a layered structure, for example, gibbsite or kaolinite (interlayer spacing 4.85 and 7.15 Å, respectively), are often encountered in MCS. For such crystalline structures intercalation of particles in the interlayer space is possible [21], and the mechanical impulse delivered facilitates this process (Fig. 4*c*). The intercalated atoms or clusters facilitate cracking of the crystals and/or formation of new compounds [12, 13].

The description of the kinetics of MCS starts from the assumption that the solid-phase interaction is accompanied by an increase in the surface of the particles as a result of dispersion, and the kinetic equation has the form [2, 3]

$$d\alpha/d\tau = K(T) f(\alpha) F(S), \qquad (1)$$

where α is the degree of transformation; τ is the process time; $K(T)$ is the effective rate constant; $f(\alpha)$ is the kinetic function; and, the function $F(S)$ describes the change in the surface area of contact between phases.

As a rule, the change in the surface $F(S)$ is described by the dispersion equation [2, 22]

$$F(S)/S_m = 1 - \exp(-k_2 \tau), \qquad (2)$$

where S_m is the maximum attainable surface of the particles under the given conditions and k_2 is the dispersion constant.

The kinetic equation of the solid-phase interaction is [2, 3]

$$f(\alpha) = x(1 - \alpha)(1 - \varepsilon\alpha), \qquad (3)$$

where x is the probability of a collision between contacting particles and the milling bodies;

$$\varepsilon = n/m;$$

n is the stoichiometric coefficient of the chemical reaction; and, m is the real molar ratio of the components.

Since MXS is, essentially, a solid-phase reaction, it is proposed in [19] that the equations of topochemical reactions, which have become classic [1], for example, the Gistling–Braunshtein equation, be used. Then the MCS Eq. (1) becomes

$$d\alpha/d\tau = K(T)[1 - \exp(-k_2 \tau)]$$
$$[1 - (1 - \alpha)^{1/3}]^{-1}(1 - \alpha)^{2/3}. \qquad (4)$$

In MCS there can arise situations where the process is not accompanied by even a slightest significant change in surface area and the reaction is accelerated as a result of deformation mixing, intercalation (especially in the case where layered minerals are used) [2 – 6, 12, 13]. Then $F(S)/S_m = 1$, and Eq. (1) becomes an equation of a first-order chemical reaction [2, 3]. In this case the equations of topochemical reactions can be used to describe the kinetics of MCS, for example, the Avraam–Erofeev equation, as in the case of MCS of sodium aluminates [20].

CONCLUSIONS

It was shown that to increase the yield and rate of synthesis of oxide compounds with covalent bonds it is best to use for MCS raw materials containing hydroxyl or different functional groups (so-called soft mechanochemistry). The effectiveness of MCS also increases with increasing difference in the acid-base properties of the surfaces of the particles of the ingredients.

It was determined that for MCS of compounds with noncovalent bonds the initial components and the conditions of synthesis must be chosen carefully so as to eliminate hydration and prevent the process from becoming 'covalent synthesis'.

Phenomenological models of MCS in systems containing components with different combinations of crystal hardness and with a layered crystal structure were discussed.

The kinetic equations for MCS, which take account of the change in the surface area of the contacting particles of the solid phase, were presented. It was proposed that the equations of topochemical reactions be used to describe the kinetics of the chemical interaction occurring in the MCS process.

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